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CRYSTALLOGRAPHIC STUDIES

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State University of New York
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Final Report
(1 November 1972 - 30 June 1976)

October 1976

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Mathematical techniques have been developed which permit the computation of hydroxyl orientations, surface energies and diffusion models for water molecules adsorbed on mineral surfaces. These have been applied to several layer silicate and related minerals.			

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STATE UNIVERSITY OF NEW YORK AT BUFFALO
Faculty of Natural Science and Mathematics
DEPARTMENT OF GEOLOGICAL SCIENCES

Final Report

October 26, 1976

Contract No. F19628-73-C-0030

R.F. Giese

A. Background

Soils are complex mixtures of fine-grained minerals and rock fragments often with admixed organic matter. The minerals are commonly clays with others which are resistant to chemical and physical weathering. It is probably true that the important chemical and physical properties of soils are due to the clay minerals present. Therefore, any knowledge or understanding of soils must ultimately rest on study of clays and clay minerals.

Many of the chemical and physical properties of clays and clay minerals which set them apart from other commonly occurring minerals result from a combination of 1) small grain size (large surface area and less than perfect crystallinity), 2) presence of interstitial water between mineral grains as well as in the mineral structure accompanied by various cations, 3) the presence of hydroxyl groups on the grain surfaces as well as in the structure and 4) a layer-type crystal structure. As a result of variations in these properties, soils are variable but a possible simplifying feature is that clays and clay minerals can be grouped into a few large families each of which should have similar properties.

A-1. Thermal Blow-Off Problem

One of the areas where the unique characteristics of clays is of prime importance is in the reaction of soils to high thermal fluxes as, for example, are experienced during an above ground nuclear explosion. Approximately one-third of the weapon output is in the form of thermal radiation from the fireball. It is well known that on many types of ground surfaces, the thermal radiation results in the ejection of dust into the air. As a result of these radiation induced changes in the surface and the first few meters above the ground, the shock wave as it propagates away from the fireball is strongly modified. The apparent heating of the atmosphere near the ground surface increases sound velocities and this results in unexpected peak pressures, directions of force and flow drag pressures. In order to accurately predict the real structure of the shock wave front, the reactions of soils to thermal radiation must be better understood.

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B. Objectives

The very nature of soil minerals and especially the clay fraction makes them very difficult to treat experimentally. An adequate understanding of their relative stability and particularly how they interact with water molecules adsorbed on the surfaces and between the layers is necessary in order to interpret and even predict experimental results. The approach adopted during this contract has been that such an understanding can be achieved by a simple theoretical treatment of clay minerals. The crystal structure of most of the important types of clay minerals are known although not always with the accuracy one would like. A complete description of these structures requires in addition a potential energy function which allows one to calculate the potential energy given the atomic positional parameters of the crystal structure.

A further aim of the research performed under this contract was to use the results of the theoretical description of clay minerals to explain the known physical and chemical properties of clays and in particular their behavior vis-a-vis adsorbed water molecules

B-1. Subtasks

In order to carry out the task outlined in the contract these subtasks were identified.

Model of Bonding

For several reasons which have been stated in previous quarterly reports, it was decided early in this research to concentrate on an ionic model for the bonding. The greatest justification for this is the simplicity of the theory and the ease and speed with which the computations may be performed using a digital computer.

The simple theory is that the atoms are fully ionized (Giese et al, Zeit. fur Krist., 134, 275-284, 1971) and that the potential energy of any such crystalline material can be calculated from

$$\frac{1}{2} \sum_i \sum_j \left[\frac{Z_i Z_j}{R_{ij}} + \frac{D_i D_j}{R_{ij}^6} + f(B_i + B_j) \exp \left(\frac{A_i + A_j - R_{ij}}{B_i + B_j} \right) \right]$$

where

Z = ionic charge

N = number of atoms in the unit cell

A, B, D = constants

f = unit force with dimensions kcal/mole/angstrom

(Busing, Trans. A.C.A., 6, 57, 1970)

The three terms in the above expression are the coulomb (electrostatic) van der Waals and repulsion energies respectively. Of the constants in these three terms, only the Z 's are known. The others must be determined using previously determined crystal structures. The process is very lengthy and has not yet been carried out. Rather, since the electrostatic energy is the largest term the research done under this contract has involved only the calculation of the electrostatic energy.

Computation

These computations have been based on a modified version of the computer program MANIOC (Baur, Zeit. fur Krist., Acta Cryst., 19, 909, 1965). All subsequent investigations of particular mineral systems has used a modular programming approach i.e. a separate program has been written for each type of investigation (interlayer bond energies, polytype stabilities, motion of water molecules, etc.) which in effect creates a series of new crystal structure representing intermediate states which occur during a physical or chemical change. The new structures are input to the program to compute the potential energy of each.

C. Results

Many of the chemical and physical properties of clays with water, organic molecules or cations involves the surface energy of the clays. This is by definition the work involved in separating the silicate layers of a clay to an infinite distance. As an initial step in this contract, work was begun on an algorithm to compute the electrostatic surface energy of any ionic crystal. This involved calculating changes in the potential energy as a function of interlayer distance (for clays and micas). This subtask was successfully completed and the algorithm applied to various sheet silicate structures (see references).

As an extension of the surface energy problem, the general question of the stability of sheet silicates was examined using the hypothesis that a stable crystal structure exists in some sort of local potential energy minimum. In particular, a stable sheet silicate should have 1) a net attractive force between the silicate layers and 2) have the layers superimposed in such a way that a translation of one layer over the other in any direction will require an input of energy. The hypothesis has been tested and verified for micas, kaolinite, dickite, nacrite, talc, pyrophyllite and several varieties of $Al(OH)_3$ (see references).

The role of hydrogen bonding has in the past often been invoked to explain the stability of the kaolin minerals and yet this was never

a very satisfactory hypothesis because the interlayer distances imply very long and therefore weak hydrogen bonds. Considerable effort went into examining this question because this is central to understanding dehydroxylation and ultimate dehydration of hydroxyl containing clays and micas. The interlayer bonding of the kaolin minerals was calculated and found to be larger whereas when F^- was substituted for OH^- in the same structures, there was found to be a small net repulsion. The sample conclusion was that the hydrogen ions were responsible for the interlayer bonding.

Finally, work was begun on the study of a dynamic system, vermiculite/water, in which the adsorbed phase is known to diffuse through the matrix. Two vermiculites were chosen, one with Na and the other with Mg as the interlayer cations because 1) much NMR work has been done on the two-layer water complex and 2) the crystal structure has been determined with reasonable accuracy. The NMR results showed that the water molecules surrounding the Na vermiculite rotate with an activation energy of 8.5 kcal/mole but the nature of the rotation was not known. Several types of rotation were considered and for each (i.e. about a vertical axis, about a 2-fold axis of the water molecule etc.) a number of models were constructed. For example in treating a rotation about a vertical axis, the atoms of the water molecules were rotated in 10° increments and in this way the dynamic process of rotation was modeled by a series of static models each representing an intermediate step in the process. The potential energy was calculated for each and the change in potential energy as a function of rotation gave the energy barrier for that particular type of motion. The one with the least activation energy was for a combined rotation about a vertical axis (to (001)) along with a rotation about the Na-O axis. The calculated energy is 10 kcal/mole in good agreement with the experimental value.

D. Publications

The following are the published results supported in whole or part by the contract. (See attached)

LIST OF PUBLICATIONS

1. A quantitative study of one-layer polytypism in the kaolin minerals, International Clay Conf., Madrid, VI, 51 (1972) (with R. Wolfe)
2. Hydroxyl orientation in pyrophyllite, Nature Phys. Science, 241, 151 (1973)
3. Hydroxyl orientations in kaolinite, dickite and nacrite, Amer. Mineral., 58, 471 (1973) (with P. Datta)
4. Interlayer bonding in kaolinite, dickite and nacrite, Clays and Clay Minerals, 21, 145 (1973)
5. Hydroxyl orientations in the muscovite polymorphs, 2M, 3T and 1M, Zeit. Krist., 137, 436 (1973) (with P. Datta)
6. Interlayer bonding in one-layer kaolin structures, Clays and Clay Minerals, 22, 137 (1974) (with R. Wolfe)
7. Surface energy calculations for muscovite, Nature Phys. Science, 248, 580 (1974)
8. Interlayer bonding in talc and pyrophyllite, Clays and Clay Minerals, 23, 165 (1975)
9. The effect of F/OH substitution on some silicate minerals, Zeit. Krist., 141, 138 (1975).
10. The location of the hydrogen in YOOH, Acta Crystallogr., B31, 1983 (1975)
11. An electron optical investigation of soil clay minerals and soil stabilizing agent interactions; AFCRL-TR-75-0374 No. 523, 14 July 1975 (with Terlecky, Wolfe and Eades)
12. The calculation of electrostatic energies of disordered crystals: columbite/ixiolite, Nature Phys. Sciences, 256, 30 (1975)
13. Hydroxyl orientations in gibbsite and bayerite, Acta Cryst. B32, 1719 (1976)
14. Hydroxyl orientations in $\text{Sr}(\text{OH})_2$, submitted to Zeit. Krist.
15. Applications of principal components analysis to the study of silicate structures; AFCRL-TR-75-0372, Environmental Research Papers, No. 521, 14 July 1975 (with C. Dentan)

16. A computer program for plotting coordination polyhedra in ionic crystals-DRWMIN; AFCRL-TR-750234, Environmental Research Papers, No. 508, 24 April 1975.
17. Crystal structures of ideal, ordered two-layer micas; AFCRL-TR-75-0471, Environmental Research Papers, No. 533, 5 September 1975
18. Crystal structures of ideal, ordered one-layer micas; AFCRL-TR-75-0838, Environmental Research Papers, No. 526, 13 August 1975.
19. A computer program for calculating the Coulomb, repulsion and van der Waals energies of ionic crystals - ENERGY; AFCRL-TR, in press.
20. Interlayer bonding in micas, Clays and Clay Minerals, submitted.